

**SEALING MATERIAL COMPOSITION FOR LIQUID CRYSTAL DISPLAY ELEMENT
AND LIQUID CRYSTAL DISPLAY ELEMENT FORMED BY USING THE SAME**

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Abstract of JP10003084

PROBLEM TO BE SOLVED: To make it possible to maintain an adequate gap by completing initial curing under specific conditions under panel pressurization and to complete post-curing under specific conditions by using a chief material contg. a specific oligomer, a hardener and an inorg. filler as essential component. **SOLUTION:** The oligomer having respectively ≥ 1 radical reactive functional groups and epoxy groups in one molecule has radical reactivity and addition reactivity by the epoxy group in combination in the molecule. The radicals generated under the conditions of 120 to 150 deg.C/5 minutes under panel pressurization react like chains and curing progresses to the extent that a cell gap can be assured. Further, the epoxy groups which hardly contribute to the reaction in the initial curing complete the addition reaction under the conditions of 150 to 250 deg.C/1 hour. The hardener contains org. peroxide and a compd. Which makes addition reaction with the epoxy groups as essential components. Further, the amt. of the inorg. filler to be added is specified to 3 to 50wt.% of the entire compsn.

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(54) 【発明の名称】 液晶表示素子用シール材組成物及びそれを用いた液晶表示素子

(57) 【要約】

【課題】 パネル加圧下で120～150℃/5分の条件で初期硬化を完了して適正ギャップを保持し、更に150～250℃/1時間という短時間の条件で後硬化を完了できることを特徴とする液晶シール材組成物を提供する。

【解決手段】 (A) 1分子中にラジカル反応性の官能基とエポキシ基とをそれぞれ一つ以上有するオリゴマーを含有する主剤、(B) 硬化剤及び(C) 無機充填材を主成分とすることを特徴とする液晶表示素子用シール材組成物。

【特許請求の範囲】

【請求項1】 (A) 1分子中にラジカル反応性の官能基とエポキシ基とをそれぞれ一つ以上有するオリゴマーを含有する主剤、(B) 硬化剤及び(C) 無機充填材を主成分とすることを特徴とする液晶表示素子用シール材組成物。

【請求項2】 ラジカル反応性の官能基がアクリロイル基及び/又はメタクリロイル基であることを特徴とする請求項1記載の液晶表示素子用シール材組成物。

【請求項3】 (B) 硬化剤が、有機過酸化物と、エポキシ基と付加反応を行う化合物とを必須成分として含有することを特徴とする請求項1記載の液晶表示素子用シール材組成物。

【請求項4】 請求項1から3のいずれか1項に記載の液晶表示素子用シール材組成物を用いた液晶表示素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は液晶表示素子用シール材組成物及びそれを用いた液晶表示素子に関するものである。

【0002】

【従来の技術】近年、軽量、薄型、低消費電力等の特徴から液晶表示素子が広く普及している。液晶表示素子は、配向処理を施された二枚のガラス、あるいはプラスチックの基板の外周部を接着剤により圧着封止しており、一般にこれを液晶表示素子用シール材（略して液晶シール材）と呼んでいる。現在、この液晶シール材は硬化物の電気的信頼性に優れることから広くエポキシ樹脂を主体としたものが用いられている（例えば特開昭59-126511号公報）。近年液晶パネルメーカーではパネルの大画面化が進行しておりこれに伴いLCDのより一層の生産性向上の努力が続けられている。従来よりもパネルサイズが大きくなるに従い、ギャップ精度保持の観点から、これまでのように貼り合わされた二枚のガラス基板を積み重ねて加熱を行う多段加圧硬化方式が困難になってきている。その結果、貼り合わされた二枚のガラス基板を一組ずつ加圧して加熱を行う枚葉硬化方式に移行されつつある。又、それに伴い液晶シール材もパネルの生産性向上の為に、従来品より短時間で硬化できるものが強く求められている。従来のシール材硬化条件はパネル加圧下で160～180℃、2時間というものが一般的であった。しかしながら、これまでのところ現状のプロセスよりも短時間硬化を追い求めたものは、従来のエポキシ樹脂を主体とした材料系に、単純にエポキシ基の開環を促す硬化促進剤を増量したものが多く、室温におけるシール材の保存安定性及び液晶が注入された後のセルの電気的信頼性（電圧保持率、残留DC電圧、消費電流値等）に劣るものが多い。又、エポキシ基が無くアクリロイル基やメタクリロイル基を持つ樹脂を用いて材料化したものについては、ラジカル硬化が試みら

れてきた。ラジカルが発生源としては、UV等により分子内開裂を引き起こしてラジカルを生成する光開始剤が用いられてきた（例えば特開昭56-53169、特開平5-295087号公報）。しかしながらシール材は系内に無機の充填材を多く含んでいるために、UV光がシール材最深部にまで透過しにくい。その為、光開始剤から十分なラジカルが供給されず結果として未反応の樹脂分が残存して液晶セルの電気的信頼性を低下させる場合が多い。又、有機過酸化物をラジカル発生源として用いて、加熱によりラジカル反応を進行させるよう材料設計をすることも可能であるが、この場合においても、依然として樹脂の硬化度が通常のエポキシ樹脂の付加反応で得られるそれよりも低い為に、シール材の接着性が不十分であったり、液晶セルの電気特性に著しい弊害を与える場合がある。このように保存性、硬化性、電気特性等が総合的にバランスのとれた速硬化性の材料は未だ上市されていない。

【0003】一方、本発明者らは、エポキシ樹脂中に単純にラジカル反応性の樹脂をブレンドしたもので材料化を行い120～150℃/5分の条件で液晶シール材の硬化を行ったところ、接着性については顕著な差は見られないものの、液晶セルの電気的信頼性が格段に低いことが判明した。この原因について詳細に検討した結果、120～150℃/5分の硬化条件で架橋に関与しなかったラジカル反応性の樹脂が液晶シール材硬化物から液晶中へブリードしていることが判明した。これに対し、分子中にラジカル反応性の官能基とエポキシ基をそれぞれ少なくとも一つ以上併せ持つオリゴマーは、たとえ架橋に関与しないアクリロイル基及びメタクリロイル基が存在しても、同一分子内にエポキシ基を保有しているために150℃～250℃/1時間の硬化条件により最終的に架橋構造に取り込まれ、樹脂が液晶中にブリードすることは無く高い電気的信頼性が得られることを見だし本発明に至った。

【0004】

【発明が解決しようとする課題】本発明は、パネル加圧下で120～150℃/5分の条件で初期硬化を完了して適正ギャップを保持し、更に150～250℃/1時間という短時間の条件で後硬化を完了できることを特徴とする液晶シール材組成物を提供するものである。

【0005】

【課題を解決するための手段】本発明は(A) 1分子中にラジカル反応性の官能基とエポキシ基とをそれぞれ一つ以上有するオリゴマーを含有する主剤、(B) 硬化剤及び(C) 無機充填材を主成分とすることを特徴とする液晶表示素子用シール材組成物である。

【0006】

【発明の実施の形態】本発明で必須成分として用いられる、1分子中にラジカル反応性の官能基とエポキシ基とをそれぞれ一つ以上有するオリゴマーは、分子中にラジ

カル反応性とエポキシ基による付加反応性を兼ね備えている。このため重合開始剤として用いられた有機過酸化物から、パネル加圧下120～150℃/5分の条件で発生したラジカルが連鎖的に反応してセルギャップが確保出来る程度まで硬化が進行する。このオリゴマーの配合量としては全樹脂中、10重量部以上100重量部以下、好ましくは20重量部以上90重量部以下、更に好ましくは30重量部以上80重量部以下である。この配合量が10重量部未満の場合にはパネル加圧下120～150℃/5分の条件で十分な初期接着力が得られず、液晶パネルのギャップが保持できず好ましくない。更に初期硬化では反応にほとんど関与しなかったエポキシ基が150℃～250℃/1時間の条件で付加反応を完了する。

【0007】本発明で用いる、1分子中にラジカル反応性の官能基とエポキシ基とをそれぞれ一つ以上有するオリゴマーにおけるラジカル反応性の官能基は、アクリロイル基及び／又はメタクリロイル基であることが好ましい。本発明で用いる、同一分子中にラジカル反応性の官能基とエポキシ基をそれぞれ少なくとも一つ以上併せ持つオリゴマーは、エポキシ基の一部を例えばアクリロイル基及び／又はメタクリロイル基により変性することにより得られる。変性前の前駆体であるエポキシ樹脂の種類については特に限定されないが、例えばビスフェノールA型エポキシ樹脂、アルキル置換ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、アルキル置換ビスフェノールF型エポキシ樹脂、ビスフェノールS型エポキシ樹脂、グリシジルアミン型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、ビフェニル型エポキシ樹脂、ナフタレン型エポキシ樹脂、ジシクロペンタジエン型エポキシ樹脂、グリシジルエステル型エポキシ樹脂、脂環式エポキシ樹脂、ウレタン変性エポキシ樹脂等がある。

【0008】硬化剤は、有機過酸化物と、エポキシ基と付加反応を行う化合物とを必須成分として含有することが好ましい。本発明で用いられる有機過酸化物は特に限定されないが、例えばジアシルパーオキサイド、パーオキシジカーボネート、パーオキシエステル、パーオキシケタール、ジアルキルパーオキサイド、ハイドロパーオキサイド等があり1種もしくは2種以上併用して用いられる。又、エポキシ基と付加反応を行う化合物としては、アミン系硬化剤、イミダゾール系硬化剤、ジシアンジアミド、ヒドラジド型硬化剤、酸無水物型硬化剤、フェノール系硬化剤等が使用可能であり、更にこれらに硬化促進剤を併用することも出来る。硬化促進剤としては、リン系化合物、3級アミン、イミダゾール系化合物、尿素型化合物等が一般に使用される。

【0009】又、無機充填材としては、例えば、各種金属の炭酸塩、アルミナ、シリカ、酸化チタン、チタン酸

カリウム等が挙げられこれらの中で種々の点からアルミナ、シリカを一種または二種以上併用して使用されることが好ましい。更に無機充填材の添加量としては、印刷性等の作業性の点から全組成物のうち3～50重量%とすることが好ましい。

【0010】又、シール材組成物の粘度調整、各成分の均一混合の目的で必要に応じて溶剤を添加しても良い。用いる種類については特に制限はないが、例えばn-ヘキサン、n-デカン、シクロヘキサン等の炭化水素系溶剤、ベンゼン、トルエン、キシレン等の芳香族系炭化水素系溶剤、ブチルアセテート、ベンジルアセテート等のエステル系溶剤、メチルセロソルブ、ブチルセロソルブ、メチルカルビトール、エチルカルビトール、ブチルカルビトール、メチルセロソルブアセテート、エチレングリコール、ジエチレングリコール、ジグリム等の多価アルコール及びその誘導体等が一種あるいは二種以上併用されて用いられる。溶剤の添加量については印刷性等の点から全組成物のうち2～50重量%とすることが好ましい。

【0011】更に、溶剤の他に必要に応じてカップリング剤、消泡剤、レベリング剤等を添加しても良い。本発明の液晶シール材を調整する際は、各成分を均一に混合させるために3本ロール等を用いて混練することが好ましい。

【0012】本発明の液晶シール材を用いて液晶表示素子を製造する方法としては、一般に以下のような方法が用いられる。先ず、液晶配向層を形成したガラス及びプラスチック基板の一方に、スクリーン印刷等の工程によりシールパターンを形成する。液晶シール材組成中に溶剤を含むために乾燥炉等で予備乾燥させた後、もう一方の基板を貼り合わせて加圧し、更に乾燥炉等で120～150℃/5分の条件で初期硬化を終えて液晶パネルの適正ギャップ保持を行う。この後、圧力を解除した状態で更に150℃/1時間の条件で後硬化を完了させる。この貼り合わせた基板に液晶を注入し、注入口をUV硬化樹脂等で封じて液晶表示素子とする。

【0013】

【実施例】以下に本発明の実施例を説明するが、本発明はこれらの実施例によって何ら限定されるものではない。

【0014】（実施例1）エポキシ樹脂としてジシクロペンタジエン型エポキシ樹脂（大日本インキ化学工業社製、HP-7200）50重量部、ビスフェノールA型エポキシ樹脂（油化シェルエポキシ社製、エビコート828）10重量部、同一分子中にアクリロイル基とエポキシ基を両末端に各々一つづつ併せ持つオリゴマー（昭和化学社製、SP-1509H）40重量部、硬化剤としてアジピン酸ジヒドラジド（以下、ADHと略す）（大塚化学社製）7重量部、有機過酸化物としてトールアルキルパーオキシベンゾエート（日本油脂社製、パーブチ

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ルZ)3重量部、硬化促進剤としてアミンダクト型ポリマー化合物であるアミキュアPN-R(味の素社製)2重量部、無機充填材として無定型シリカ(日本アエロジル社製、アエロジルR-972)5重量部、アルミナ(昭和電工社製、UA-5105)30重量部、溶剤としてエチルジグリム15重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。

【0015】次に、この接着剤組成物に直径6 μ mのロッド状スペーサーを1%混合し、以下の要領で液晶セルを作製した。

(スクリーン印刷)300メッシュの版を用いて配向膜を形成させたITO付きガラス基板上(一辺3cmの正方形)に線幅が0.3mmの正方形のパターンをスクリーン印刷した。

(予備乾燥)熱風乾燥中、90℃/30分予備乾燥した。

(貼り合わせ/加熱硬化)配向膜を形成させたITO付*

きガラス基板を、配向方向がシール材を印刷した基板の配向処理方向に対して90度になるように貼り合わせ、1kg/cm²の圧力をかけた状態で熱風乾燥機中140℃/5分初期硬化させた。これを室温まで冷却し、圧力を解除した状態で150℃/1時間、後硬化を行った。尚、評価セルは各n=10作製した。

(液晶注入/封口)フッ素系液晶(メルク社製、ZLI-4792)を注入し、注入口をアクリル系UV硬化樹脂で封口した。

10 【0016】評価は次のように行った。125℃/2.3atmに設定したプレッシャークーラー試験器に12hr、上記液晶表示素子を放置。処理が終わった後、この液晶セルの電圧保持率及びシール部分の剥離の有無を確認した。評価の結果は表1に示す通りである。

【0017】

【表1】

| | 電圧保持率(%) | シール部剥離の有無 |
|------|----------|-----------|
| 実施例1 | 98 | 無し |
| 実施例2 | 98 | 無し |
| 実施例3 | 98 | 無し |
| 比較例1 | 82 | 有り |
| 比較例2 | 85 | 有り |
| 比較例3 | 83 | 有り |

【0018】(実施例2)エポキシ樹脂としてジシクロペンタジエン型エポキシ樹脂(大日本インキ化学工業社製、HP-7200)40重量部、ビスフェノールA型エポキシ樹脂(油化シェルエポキシ社製、エビコート1001)20重量部、同一分子中にアクリロイル基とエポキシ基を両末端に各々一つずつ併せ持つオリゴマー(昭和高分子社製、SP-1509H)40重量部、硬化剤としてADH(大塚化学社製)7重量部、有機過酸化物としてクメンハイドロパーオキサイド(日本油脂社製、パークミルH)4重量部、硬化促進剤としてアミンダクト型ポリマー化合物であるアミキュアMY-R(味の素社製)2重量部、無機充填材として無定型シリカ(日本アエロジル社製、アエロジルR-972)5重量部、アルミナ(昭和電工社製、UA-5105)30重量部、溶剤としてエチルジグリム20重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。評価の結果は表1に示す通りである。

【0019】(実施例3)エポキシ樹脂としてナフタレン型エポキシ樹脂(大日本インキ化学工業社製、HP-4032)40重量部、ビスフェノールA型エポキシ樹脂(油化シェルエポキシ社製、エビコート1001)20重量部、同一分子中にメタクリロイル基とエポキシ基

30 を両末端に各々一つずつ併せ持つオリゴマー(日本油脂社製、ブレンマーGH)40重量部、硬化剤としてジシアンジアミド(日本カーバイド社製)10重量部、有機過酸化物としてト-ブチルパーオキシ2-エチルヘキサノエート(日本油脂社製、バーブチルO)4重量部、硬化促進剤としてアミンダクト型ポリマー化合物であるアミキュアMY-R(味の素社製)2重量部、無機充填材として無定型シリカ(日本アエロジル社製、アエロジルR-972)5重量部、アルミナ(昭和電工社製、UA-5105)30重量部、溶剤としてエチルジグリム20重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。評価の結果は表1に示す通りである。

40 【0020】(比較例1)エポキシ樹脂としてジシクロペンタジエン型エポキシ樹脂(大日本インキ化学工業社製、HP-7200)50重量部、ビスフェノールA型エポキシ樹脂(油化シェルエポキシ社製、エビコート828)10重量部、3-シクロヘキセニルメチルアクリレート(ダイセル工業社製、CHAA)40重量部、硬化剤としてADH(大塚化学社製)7重量部、有機過酸化物としてト-ブチルパーオキシベンゾエート(日本油脂社製、バーブチルZ)3重量部、硬化促進剤としてア

ミンアダクト型ポリマー化合物であるアミキュアPN-R（味の素社製）2重量部、無機充填材として無定型シリカ（日本アエロジル社製、アエロジルR-972）5重量部、アルミナ（昭和電工社製、UA-5105）30重量部、溶剤としてエチルジグリム15重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。

【0021】（比較例2）エポキシ樹脂としてジシクロペンタジエン型エポキシ樹脂（大日本インキ化学工業社製、HP-7200）40重量部、ビスフェノールA型エポキシ樹脂（油化シェルエポキシ社製、エビコート1001）20重量部、末端にカルボキシル基を有するラクトン変性アクリレート（ダイセル化学工業社製、ブラクセルFM1A）40重量部、硬化剤としてADH（大塚化学社製）7重量部、有機過酸化物としてクメンハイドロパーオキサイド（日本油脂社製、パークミルH）4重量部、硬化促進剤としてアミンアダクト型ポリマー化合物であるアミキュアMY-R（味の素社製）2重量部、無機充填材として無定型シリカ（日本アエロジル社製、アエロジルR-972）5重量部、アルミナ（昭和電工社製、UA-5105）30重量部、溶剤としてエチルジグリム20重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。評価の結果は表1に示す通りである。

【0022】（比較例3）エポキシ樹脂としてナフタレン型エポキシ樹脂（大日本インキ化学工業社製、HP-4032）40重量部、ビスフェノールA型エポキシ樹脂（油化シェルエポキシ社製、エビコート1001）20重量部、アリルメタクリレート（ダイセル化学工業社製、ALMA）40重量部、硬化剤としてジシアンジアミド（日本カーバイド社製）10重量部、有機過酸化物としてt-ブチルパーオキシ 2-エチルヘキサノエート（日本油脂社製、パーブチルO）4重量部、硬化促進剤としてアミンアダクト型ポリマー化合物であるアミキュアMY-R（味の素社製）2重量部、無機充填材として無定型シリカ（日本アエロジル社製、アエロジルR-972）5重量部、アルミナ（昭和電工社製、UA-5105）30重量部、溶剤としてエチルジグリム20重量部を攪拌混合し、更に三本ロールで十分に混練して接着剤組成物を得た。評価の結果は表1に示す通りである。

【0023】

【発明の効果】本発明によれば、パネル加圧下で120～150℃/5分の条件で初期硬化を完了して適正ギャップを保持し、更に150～250℃/1時間という短時間の条件で後硬化を完了でき液晶パネルの生産性向上を図ることが出来る。

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(54) SEALING MATERIAL COMPOSITION FOR LIQUID CRYSTAL DISPLAY ELEMENT, AND LIQUID CRYSTAL DISPLAY ELEMENT FORMED BY USING THE SAME**(57)Abstract:**

PROBLEM TO BE SOLVED: To make it possible to maintain an adequate gap by completing initial curing under specific conditions under panel pressurization and to complete post-curing under specific conditions by using a chief material contg. a specific oligomer, a hardener and an inorg. filler as essential component.

SOLUTION: The oligomer having respectively ≥ 1 radical reactive functional groups and epoxy groups in one molecule has radical reactivity and addition reactivity by the epoxy group in combination in the molecule. The radicals generated under the conditions of 120 to 150° C/5 minutes under panel pressurization react like chains and curing progresses to the extent that a cell gap can be assured. Further, the epoxy groups which hardly contribute to the reaction in the initial curing complete the addition reaction under the conditions of 150 to 250° C/1 hour. The hardener contains org. peroxide and a compd. Which makes addition reaction with the epoxy groups as essential components. Further, the amt. of the inorg. filler to be added is specified to 3 to 50wt.% of the entire compsn.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The sealant constituent for liquid crystal display components characterized by using as a principal component the base resin, the (B) curing agent, and (C) inorganic filler containing the oligomer which has one or more the functional groups and epoxy groups of radical reaction nature in 1 molecule, respectively.

[Claim 2] The sealant constituent for liquid crystal display components according to claim 1 characterized by the functional groups of radical reaction nature being an acryloyl radical and/or a methacryloyl radical.

[Claim 3] (B) The sealant constituent for liquid crystal display components according to claim 1 characterized by a curing agent containing organic peroxide, and an epoxy group and the compound which performs an addition reaction as an indispensable component.

[Claim 4] The liquid crystal display component using the sealant constituent for liquid crystal display components given in any 1 term of claims 1-3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the liquid crystal display component which used the sealant constituent for liquid crystal display components, and it.

[0002]

[Description of the Prior Art] In recent years, the liquid crystal display component has spread widely from the descriptions, such as a light weight, a thin shape, and a low power. The liquid crystal display component is carrying out sticking-by-pressure closure of the periphery section of the substrate of the glass of two sheets to which orientation processing was performed, or plastics with adhesives, and, generally is calling this the sealant for liquid crystal display components (omitting liquid crystal sealant). What made the epoxy resin the subject widely from current and this liquid crystal sealant being excellent in the electric dependability of a hardened material is used (for example, JP.59-126511A). By the liquid crystal panel manufacturer, big screen-ization of a panel is advancing and efforts of much more productivity drive of LCD are continued in connection with this in recent years. The multistage pressurization hardening method which heats from a viewpoint of gap precision maintenance by accumulating two glass substrates stuck like the former is becoming difficult as panel size becomes large conventionally. Consequently, it is shifting to the sheet hardening method which heats by pressurizing two stuck glass substrates a lot every. Moreover, what can also harden a liquid crystal sealant from elegance conventionally in connection with it in a short time for the productivity drive of a panel is called for strongly. The conventional sealant hardening conditions had the common thing of 160-180 degrees C and 2 hours under panel pressurization. However, there is much what pursued short-time hardening rather than the present process the old place about what increased the quantity of the hardening accelerator which urges the ring breakage of an epoxy group to the ingredient system which made the conventional epoxy resin the subject simply, and there are many things inferior to the electric dependability (electrical-potential-difference retention, a residual DC electrical potential difference, consumed-electric-current value, etc.) of the cel after the preservation stability and liquid crystal of a sealant in a room temperature were poured in. Moreover, radical hardening has been tried about what was ingredient-ized using the resin which there is no epoxy group and has an acryloyl radical and a methacryloyl radical. The photoinitiator which causes intramolecular cleavage by UV etc. and generates a radical as a generation source of a radical has been used (for example, JP.58-53189A, JP.5-259087A). However, since the sealant contains many inorganic fillers in the system, UV light cannot penetrate it easily even to the sealant deepest part. For the reason, sufficient radical is not supplied from a photoinitiator, but a pitch unreacted as a result remains, and the electric dependability of a liquid crystal cell is reduced in many cases. Moreover, since whenever [hardening / of resin] is also in this case still lower than it which is obtained by the addition reaction of the usual epoxy resin although it is also possible to carry out a materials design so that radical reaction may be advanced with heating, using organic peroxide as a radical generation source, the adhesive property of a sealant may be inadequate or remarkable evil may be done to the electrical property of a liquid crystal cell. Thus, Kamichi of the ingredient of fast

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epoxy resin, a glycidyl ester mold epoxy resin, cycloaliphatic epoxy resin, an urethane modified epoxy resin, etc.

[0008] As for a curing agent, it is desirable to contain organic peroxide, and an epoxy group and the compound which performs an addition reaction as an indispensable component, although especially the organic peroxide used by this invention is not limited — for example, diacyl peroxide, peroxy dicarbonate, peroxy ester, peroxy ketal, dialkyl peroxide, hydroperoxide, etc. — it is — one sort — or two or more sorts are used together and it is used. Moreover, as a compound which performs an epoxy group and an addition reaction, an amine system curing agent, an imidazole system curing agent, a dicyandiamide, a hydrazide mold-curing agent, an acid-anhydride mold-curing agent, a phenol system curing agent, etc. are usable, and a hardening accelerator can also be further used together to these. Generally as a hardening accelerator, the Lyrn system compound, tertiary amine, an imidazole system compound, a urea mold compound, etc. are used.

[0009] Moreover, as an inorganic filler, for example, the carbonate of various metals, an alumina, a silica, titanium oxide, potassium titanate, etc. are mentioned, and it is desirable a kind or to use an alumina and a silica for two or more sorts from various points in these, using together. Furthermore, as an addition of an inorganic filler, it is desirable to consider as 3 ~ 50 % of the weight in all constituents from the point of workability, such as printing nature.

[0010] Moreover, a solvent may be added if needed for the viscosity control of a sealant constituent, and the purpose of homogeneity mixing of each component, although there is especially no limit about the class to be used — polyhydric alcohol, such as ester solvents, such as aromatic series system hydrocarbon system solvents, such as hydrocarbon system solvents, such as for example, n-hexane, n-Decane, and a cyclohexane, benzene, toluene, and a xylene, butyl acetate, and benzyl acetate, methyl cellosolve, butyl cellosolve, methyl carbitol, ethyl carbitol, butyl carbitol, methyl-cellosolve acetate, ethylene glycol, a diethylene glycol, and a jig lime the derivative of those, etc. — a kind — or two or more sorts be used together and it be used. About the addition of a solvent, it is desirable to consider as 2 ~ 50 % of the weight in all constituents from points, such as printing nature.

[0011] Furthermore, a coupling agent, a defoaming agent, a leveling agent, etc. may be added if needed other than a solvent. In case the liquid crystal sealant of this invention is adjusted, in order to make homogeneity mix each component, it is desirable to use and knead 3 rolls etc.

[0012] Generally as an approach of manufacturing a liquid crystal display component using the liquid crystal sealant of this invention, the following approaches are used. First, a seal pattern is formed in either the glass in which the liquid crystal orientation layer was formed, or a plastic plate, according to processes, such as screen-stencil. Since a solvent is included during a liquid crystal sealant presentation, after carrying out predrying with a drying furnace etc., another substrate is stuck, and is pressurized, an initial set is further finished with a drying furnace etc. on the conditions for 120-150 degrees C / 5 minutes, and proper gap maintenance of a liquid crystal panel is performed. Then, posture is made to complete on the conditions of 150 more degrees C / 1 hour, where a pressure is canceled. Liquid crystal is injected into this stuck substrate, UV hardening resin etc. stops an inlet, and it considers as a liquid crystal display component.

[0013]

[Example] Although the example of this invention is explained below, this invention is not limited at all by these examples.

[0014] (Example 1) as an epoxy resin — a dicyclopentadiene mold epoxy resin (the Dainippon Ink & Chemicals, Inc. make —) the HP-7200 50 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the oligomer (the Showa High Polymer Co., Ltd. make —) even each has oligomer and an acryloyl radical and an epoxy group every in both ends in the Epicoat 828 10 weight section and the same molecule As the SP-1509H 40 weight section and a curing agent, adipic-acid dihydrazide (It abbreviates to ADH hereafter) as 7 weight sections and organic peroxide — t-butyl peroxybenzoate (the Otsuka chemistry company make) (the Nippon Oil & Fats Co., Ltd. make —) The par butyl 23 weight section, the friend cure PH-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a

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curability with which shelf life, hardenability, an electrical property, etc. maintained balance synthetically is not yet carried out.

[0003] On the other hand, although the difference remarkable about an adhesive property was not seen when this invention persons are what blended the resin of radical reaction nature simply in the epoxy resin, and performed ingredient-ization and the liquid crystal sealant was hardened on the conditions for 120-150 degrees C / 5 minutes, it became clear that the electric dependability of a liquid crystal cell is alike and low. As a result of considering this cause in a detail, it became clear that the resin of the radical reaction nature which did not participate in bridge formation on the hardening conditions for 120-150 degrees C / 5 minutes was carrying out bleeding into liquid crystal from the liquid crystal sealant hardened material. On the other hand, the oligomer which has at least one or more the functional groups and epoxy groups of radical reaction nature in a molecule, respectively Even if the acryloyl radical and methacryloyl radical which do not participate in bridge formation even if exist it found out that are finally incorporated by the structure of cross linkage according to the hardening conditions of 150 degrees C ~ 250 degrees C / 1 hour since the epoxy group is held in the same intramolecular, and resin did not carry out bleeding into liquid crystal, and high electric dependability was acquired, and resulted in this invention.

[0004]

[Problem(s) to be Solved by the Invention] This invention completes an initial set under panel pressurization on the conditions for 120-150 degrees C / 5 minutes, holds a proper gap, and offers the liquid crystal sealant constituent characterized by the ability to complete posture on condition that a short time of further 150-250 degrees C / 1 hour.

[0005]

[Means for Solving the Problem] This invention is a sealant constituent for liquid crystal display components characterized by using as a principal component the base resin, the (B) curing agent, and (C) inorganic filler containing the oligomer which has one or more the functional groups and epoxy groups of radical reaction nature in (A) molecule, respectively.

[0006]

[Embodiment of the Invention] The oligomer which is used as an indispensable component by this invention and which has one or more the functional groups and epoxy groups of radical reaction nature in 1 molecule, respectively combines radical reaction nature and the addition reaction nature by the epoxy group in the molecule. For this reason, hardening advances to extent which the radical generated on the conditions for bottom 120-150 degrees C / of panel pressurization, and 5 minutes reacts continuously, and can secure the GYAPU from the organic peroxide used as a polymerization initiator. As loadings of this oligomer, they are below 80 weight sections more than 30 weight sections still more preferably below 90 weight sections more than 20 weight sections preferably below the 100 weight sections more than 10 weight sections among [all] resin. When these loadings are under 10 weight sections, initial adhesive strength sufficient on the conditions for bottom 120-150 degrees C / of panel pressurization, and 5 minutes is not obtained, the gap of a liquid crystal panel cannot be held, and it is not desirable. Furthermore, at an initial set, the epoxy group which hardly participated in a reaction completes an addition reaction on the conditions of 150 degrees C ~ 250 degrees C / 1 hour.

[0007] As for the functional group of the radical reaction nature in the oligomer which has one or more the functional groups and epoxy groups of radical reaction nature in 1 molecule, respectively used by this invention, it is desirable that they are an acryloyl radical and/or a methacryloyl radical. The oligomer which is used by this invention and which has at least one or more the functional groups and epoxy groups of radical reaction nature in the same molecule, respectively is obtained by denaturalizing by for example, the acryloyl radical and/or the methacryloyl radical in a part of epoxy group. Although not limited especially about the class of epoxy resin which is a precursor before denaturation For example, the bisphenol A mold epoxy resin, an alkylation bisphenol A mold epoxy resin, A bisphenol female mold epoxy resin, an alkylation bisphenol female mold epoxy resin, A bisphenol smooth S form epoxy resin, a glycidyl amine mold epoxy resin, A phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, There are a biphenyl mold epoxy resin, a naphthalene mold epoxy resin, a dicyclopentadiene mold

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hardening accelerator, The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 15 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives - constituent was obtained.

[0015] Next, the rod-like spacer with a diameter of 6 micrometers was mixed 1% to this adhesives constituent, and the liquid crystal cell was produced in the following ways. (Screen-stencil) Line breadth screen-stenciled the pattern of the square which is 0.3mm on the glass substrate with ITO in which the orientation film was made to form using the version of 300 meshes (one-side square of 3cm).

(Predrying) Predrying was carried out during hot air drying for 90 degrees C / 30 minutes. (Lamination/heat hardening) Where lamination and the pressure of 1kg/cm2 are put for the direction of orientation to become 90 degrees to the orientation processing direction of the substrate which printed the sealant about the glass substrate with ITO in which the orientation film was made to form, the initial set was carried out for 140 degrees C in hot air drying equipment / 5 minutes. This was cooled to the room temperature, and where a pressure is canceled, posture was performed for 150 degrees C / 1 hour. In addition, the evaluation cel was produced each n=10.

(Liquid crystal impregnation / obturation) Fluorine system liquid crystal (the Merck Co. make, ZLI-4792) was poured in, and the inlet was obturated with acrylic UV hardening resin.

[0016] Evaluation was performed as follows. 12w(s) and the above-mentioned liquid crystal display component are left in the pressure cooker tester set as 125 degree-C/2.3atm. After processing finished, the electrical-potential-difference retention of this liquid crystal cell and the existence of exfoliation of a seal part were checked. The result of evaluation is as being shown in Table 1.

[0017]

(Table 1)

| | 電圧保持率 (%) | シール部剥離の有無 |
|-------|-----------|-----------|
| 実例 1 | 98 | 無し |
| 実例 2 | 98 | 無し |
| 実例 3 | 98 | 無し |
| 比較例 1 | 82 | 有り |
| 比較例 2 | 85 | 有り |
| 比較例 3 | 83 | 有り |

[0018] (Example 2) as an epoxy resin — a dicyclopentadiene mold epoxy resin (the Dainippon Ink & Chemicals, Inc. make —) the HP-7200 40 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the oligomer (the Showa High Polymer Co., Ltd. make —) even each has oligomer and an acryloyl radical and an epoxy group every in both ends in the Epicoat 1001 20 weight section and the same molecule As the SP-1509H 40 weight section and a curing agent, the ADH(Otsuka chemistry company make) 7 weight section, as organic peroxide — a cumene hydroperoxide (the Nippon Oil & Fats Co., Ltd. make —) The Park Mill H4 weight section, the friend cure MY-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a hardening accelerator. The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 20 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives constituent was obtained. The result of evaluation is as being shown in Table 1.

[0019] (Example 3) as an epoxy resin — a naphthalene mold epoxy resin (the Dainippon Ink &

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Chemicals, Inc. make —) the HP-4032 40 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the oligomer (the Nippon Oil & Fats Co., Ltd. make —) even each has oligomer and a methacryloyl radical and an epoxy group every in both ends in the Epicoat 1001 20 weight section and the same molecule As the BUREMMA GH40 weight section and a curing agent, the dicyandiamide (Japanese carbide company make) 10 weight section, as organic peroxide — tert-butyl peroxide 2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make —) The par butyl O4 weight section, the friend cure MY-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a hardening accelerator, The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 20 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives constituent was obtained. The result of evaluation is as being shown in Table 1.

[0020] (Example 1 of a comparison) as an epoxy resin — a dicyclopentadiene mold epoxy resin (the Dainippon Ink & Chemicals, Inc. make —) the HP-7200 50 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the Epicoat 828 10 weight section and 3-cyclohexenyl methyl acrylate (die cel industrial company make —) As the CHAA40 weight section and a curing agent, the ADH(Otsuka chemistry company make) 7 weight section, as organic peroxide — t-butyl peroxybenzoate (the Nippon Oil & Fats Co., Ltd. make —) The par butyl Z3 weight section, the friend cure PN-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a hardening accelerator, The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 15 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives constituent was obtained.

[0021] (Example 2 of a comparison) as an epoxy resin — a dicyclopentadiene mold epoxy resin (the Dainippon Ink & Chemicals, Inc. make —) the HP-7200 40 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the lactone denaturation acrylate (the Daicel Chemical Industries, Ltd. make —) which has a carboxyl group at the Epicoat 1001 20 weight section and the end As the plaque cel FM1A40 weight section and a curing agent, the ADH(Otsuka chemistry company make) 7 weight section, as organic peroxide — a cumene hydroperoxide (the Nippon Oil & Fats Co., Ltd. make —) The Park Mill H4 weight section, the friend cure MY-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a hardening accelerator, The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 20 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives constituent was obtained. The result of evaluation is as being shown in Table 1.

[0022] (Example 3 of a comparison) as an epoxy resin — a naphthalene mold epoxy resin (the Dainippon Ink & Chemicals, Inc. make —) the HP-4032 40 weight section and the bisphenol A mold epoxy resin (oil-ized shell epoxy company make —) the Epicoat 1001 20 weight section and allyl compound methacrylate (the Daicel Chemical Industries, Ltd. make —) As the ALMA40 weight section and a curing agent, the dicyandiamide (Japanese carbide company make) 10 weight section, as organic peroxide — tert-butyl peroxide 2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make —) The par butyl O4 weight section, the friend cure MY-R(Ajinomoto Co., Inc. make) 2 weight section which is an amine adduct mold polymer compound as a hardening accelerator, The non-fixed form silica (product [made from Japanese Aerosil], Aerosil R-972) 5 weight section and the alumina (Showa Denko K.K. make, UA-5105) 30 weight section were carried out as an inorganic filler, stirring mixing of the ethyl jig lime 20 weight section was carried out as a solvent, it fully kneaded with 3 more roll, and the adhesives constituent was obtained. The result of evaluation is as being shown in Table 1.

[0023]

[Effect of the Invention] According to this invention, an initial set is completed under panel pressurization on the conditions for 120-150 degrees C / 5 minutes, a proper gap can be held,

postcure can be completed on condition that a short time of further 150-250 degrees C / 1 hour, and the productivity drive of a liquid crystal panel can be planned.

[Translation done.]